

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6747/STA-144

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

10/009543
To Be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/03684

25 April 2000 (25.04.00)

07 May 1999 (7.05.99)

TITLE OF INVENTION

METHOD FOR PRODUCING NICKEL HYDROXIDES

APPLICANT(S) FOR DO/EO/US OLBRICH, Armin; STOLLER, Viktor; MEESE-MARKTSCHIEFFEL, Juliane;
SCHRUMPF, Frank; SCHMOLL, Josef and GILLE, Gerhard

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Form PTO 1449 w/references
Drawings (4 sheets)

APPLICATION NO (if known, see 37 CFR 1.5)
 To Be Assigned **09543**

INTERNATIONAL APPLICATION NO
PCT/EP00/03684

ATTORNEY'S DOCKET NUMBER
Mo-6747/STA-144

21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
 and International Search Report not prepared by the EPO or JPO. **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to
 USPTO but International Search Report prepared by the EPO or JPO **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ **890.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ **0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	13 - 20 =	0	x \$18.00	\$ 0.00	
Independent claims	1 - 3 =	0	x \$84.00	\$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS = \$ **890.00**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
 are reduced by 1/2. + \$ **0.00**

SUBTOTAL = \$ **890.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ **0.00**

TOTAL NATIONAL FEE = \$ **890.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ **40.00**

TOTAL FEES ENCLOSED = \$ **930.00**

Amount to be
 refunded: \$
 charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 930.00 to cover the above fees.
 A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card: **WARNING:** Information on this form may become public. **Credit card
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



00157

PATENT TRADEMARK OFFICE

SIGNATURE

Diderico van Eyl

NAME

38,641

REGISTRATION NUMBER

PATENT APPLICATION
Mo-6747
STA-144

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
ARMIN OLBRICH ET AL) PCT/EP00/03684
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: PROCESS FOR THE PRODUCTION)
OF NICKEL HYDROXIDES)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the subject application and before assigning a serial number, please amend the application as follows:

"Express Mail" mailing label number ET700176854US
Date of Deposit November 5, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee)

IN THE CLAIMS:

Please cancel Claims 1-12 and add new Claims 13-25:

--13. A process for producing spherical nickel hydroxide comprising:

(a) subjecting a nickel electrode to anodic dissolution in a completely intermixed electrolysis cell and using an electrolysis brine that is introduced into the cell and that has (i) a chlorine ion content ranging from 20 to 50 g/l (ii) an ammonia content ranging from 1 to 7 g/l of (iii) a pH value ranging from 9.5 to 11.5 and (iv) a temperature of 45 to 60°C; and

(b) precipitating nickel hydroxide.

14. The process according to Claim 13, wherein before introducing the electrolysis brine into the electrolysis cell, the pH of the electrolysis brine is adjusted to a value ranging from 10 to 10.5 by addition of alkali metal hydroxide or hydrochloric acid to the brine.

15. The process according to Claim 13, wherein the brine has a circulation rate that is at least 20 cm/s.

16. The process according to Claim 13, wherein the molar ratio of chloride ions to ammonia is from 2 to 10.

17. The process according to Claim 13, wherein the electrolysis brine has an average residence time ranging from 1 to 5 hours.

18. The process according to Claim 13 further comprising continuously introducing into the electrolysis cell a doping metal ion selected from the group consisting of Co, Zn, Mg, Cu, Cr, Fe, Sc, Y, La, lanthanoids, B, Ga, Mn, Cd and Al.

19. The process according to Claim 18, wherein the doping element ions are produced by anodic oxidation of the corresponding metals.

20. The process according to Claim 13 further comprising discharging brine containing dispersed nickel hydroxide powder from the electrolysis cell, separating nickel hydroxide powder and returning the brine to the electrolysis cell.

21. The process according to Claim 13 further comprising discharging brine containing dispersed nickel hydroxide powder from the electrolysis cell and introducing the brine containing dispersed nickel hydroxide into a downstream electrolysis cell having a metallic cobalt anode.

22. The process according to Claim 21 further comprising discharging brine containing nickel hydroxide powder coated with cobalt hydroxide from the electrolysis cell containing metallic cobalt, separating the nickel hydroxide powder and returning the brine to the electrolysis cell.

23. A nickel hydroxide powder made by Claim 13.

24. The nickel hydroxide powder of Claim 23, wherein the powder is an electrode material of a secondary storage battery.

25. The nickel hydroxide powder of Claim 23, wherein the powder is a precursor material for the production of an ultrafine powdered metallic nickel.--

IN THE SPECIFICATION

On page 1, below the Title, please add:

--This application is the National Stage Application of PCT/EP00/03684, which claims a priority from German Application 199 21 313.5, filed May 7, 1999.

BACKGROUND--

On page 2, line 20, please add:

--DESCRIPTION--

On page 8, line 3, please add:

--The invention is further described in the following illustrative examples in which all parts and percentages are by weight unless otherwise indicated.--

On page 9, below line 30, please add:

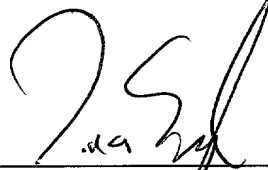
--Although the present invention has been described in detail with reference to certain preferred versions thereof, other variations are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the versions contained therein. --

REMARKS

Entry of this Preliminary Amendment is requested. The above-made modifications have been made to place the application in conformance with U.S. standards. No new matter has been added.

Respectfully submitted,

By



Diderico van Eyl
Attorney for Applicants
Reg. No. 38,641

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-8355
FACSIMILE PHONE NUMBER:
(412) 777-8363

s:/sr/dve0399

MARKED-UP VERSION SHOWING MODIFICATIONS

Please cancel Claims 1-12 and add new Claims 13-25:

--13. A process for producing spherical nickel hydroxide comprising:

(a) subjecting a nickel electrode to anodic dissolution in a completely intermixed electrolysis cell and using an electrolysis brine that is introduced into the cell and that has (i) a chlorine ion content ranging from 20 to 50 g/l (ii) an ammonia content ranging from 1 to 7 g/l of (iii) a pH value ranging from 9.5 to 11.5 and (iv) a temperature of 45 to 60°C; and

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16. The process according to Claim 13, wherein the molar ratio of chloride ions to ammonia is from 2 to 10.

17. The process according to Claim 13, wherein the electrolysis brine has an average residence time ranging from 1 to 5 hours.

18. The process according to Claim 13 further comprising continuously introducing into the electrolysis cell a doping metal ion selected from the group consisting of Co, Zn, Mg, Cu, Cr, Fe, Sc, Y, La, lanthanoids, B, Ga, Mn, Cd and Al.

19. The process according to Claim 18, wherein the doping element ions are produced by anodic oxidation of the corresponding metals.

20. The process according to Claim 13 further comprising discharging brine containing dispersed nickel hydroxide powder from the electrolysis cell, separating nickel hydroxide powder and returning the brine to the electrolysis cell.

21. The process according to Claim 13 further comprising discharging brine containing dispersed nickel hydroxide powder from the electrolysis cell and introducing the brine containing dispersed nickel hydroxide into a downstream electrolysis cell having a metallic cobalt anode.

22. The process according to Claim 21 further comprising discharging brine containing nickel hydroxide powder coated with cobalt hydroxide from the electrolysis cell containing metallic cobalt, separating the nickel hydroxide powder and returning the brine to the electrolysis cell.

23. A nickel hydroxide powder made by Claim 13.

24. The nickel hydroxide powder of Claim 23, wherein the powder is an electrode material of a secondary storage battery.

25. The nickel hydroxide powder of Claim 23, wherein the powder is a precursor material for the production of an ultrafine powdered metallic nickel.--

IN THE SPECIFICATION

On page 1, below the Title, please add:

--This application is the National Stage Application of PCT/EP00/03684, which claims a priority from German Application 199 21 313.5, filed May 7, 1999.

BACKGROUND--

On page 2, line 20, please add:

--DESCRIPTION--

On page 8, line 3, please add:

--The invention is further described in the following illustrative examples in which all parts and percentages are by weight unless otherwise indicated.--

On page 9, below line 30, please add:

--Although the present invention has been described in detail with reference to certain preferred versions thereof, other variations are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the versions contained therein. --

Process for the production of nickel hydroxides

This invention relates to a process for the production of nickel hydroxides by anodic dissolution of metallic nickel in an electrolysis cell with completely intermixed electrolysis brine.

Two processes are in particular known for the production of nickel hydroxides, namely chemical precipitation of the hydroxides from nickel salt solutions by addition of alkali metal hydroxide solutions and, secondly, anodic dissolution of nickel in an electrolysis cell, wherein hydrogen is liberated at the cathode providing the corresponding hydroxide ions.

The chemical precipitation process has the disadvantage that the neutral salts produced in stoichiometric quantities from the neutralisation reaction must be disposed of or worked up. In contrast, in electrolytic processes, it is largely possible to circulate the brine containing conductive salts by separating the precipitated hydroxide, such that the formation of secondary and waste products may largely be avoided. At least in theory, electrolytic processes should give rise to more uniform products due to the lower concentrations of the reaction partners in the precipitation suspension (electrolysis brine). However, electrolytic processes do disadvantageously exhibit a tendency towards forming anodic and/or cathodic deposits or deposits on optionally present diaphragms or membranes due to the great variations in concentration, potential and/or pH values prevailing at the corresponding boundary layers, so hindering the establishment and maintenance of process conditions which are optimal with regard to product properties or which even prevent the electrolysis from being operated at equilibrium.

It is furthermore known, for example from Japanese published patent application 56-143 671 dated 9 November 1981, to produce denser nickel hydroxide powders by performing chemical precipitation from aqueous solutions of nickel ammine

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Donna J. Veatch

(Name of person mailing paper or fee)

Donna J. Veatch
Signature of person mailing paper or fee

complex salts from which nickel hydroxide precipitates at a substantially reduced precipitation rate, such that a denser particle structure is formed. Moreover, the modified crystallisation/solution equilibrium brought about by the presence of ammonia in the precipitation solution favours the formation of spheroidal agglomerates.

If the complexing agent is used in the electrolytic process, the process may be disrupted as Ni(II) in Ni(II) ammine complexes is more readily cathodically reduced than in the Ni(II) hexaaquo complex ion. The precipitated Ni forms loose deposits on the cathode. This problem is remedied according to EP-A-684 324 by dividing the electrolysis cell into an anode compartment and a cathode compartment by means of a membrane permeable to hydroxide ions. In order to avoid the formation of nickel hydroxide deposits both on the membrane and on the anode, it is necessary in this process to use very high ammonia concentrations, such that the hydroxide precipitates with an increase in temperature only once it has left the reactor. Disadvantages of the membrane electrolysis process include the increased electrolysis voltage entailed by the membrane and the use of the membrane itself which is technically problematic (clogging problems), increases process costs and thus complicates commercial application.

It has now been found that spherical nickel hydroxide may be produced by anodic dissolution of nickel directly in a completely intermixed electrolysis cell if the electrolysis brine exhibits comparatively low ammonia contents of 1 to 5 g/l and moreover the chloride ion content, pH value and temperature of the brine are maintained within certain limits.

It is apparently essential to the process according to the invention for a quasi steady-state deposit of basic nickel salt to form on the anode, which clearly assumes the function of a cation exchange membrane, *i.e.* is impermeable to chloride and hydroxide ions. The anodically dissolved nickel ions collide with the deposit from the anode side and are incorporated therein as basic nickel chloride. Nickel

ammonium complexes which have fewer than 4 ligands and are thus relatively unstable, are obviously dissolved from the electrolyte side. Formation of the ammine complex is here apparently favoured by a boundary layer which forms on the electrolyte side of the "membrane" and, in comparison with the brine concentration, has a low OH ion content. On leaving the boundary layer with a low OH ion content, the ammine complexes dissociate before nickel is deposited on the cathode.

The present invention accordingly provides a process for the production of spherical nickel hydroxide by anodic dissolution of a nickel electrode and precipitation of nickel hydroxide in a completely intermixed electrolysis cell, which process is characterised in that that an electrolysis brine is used which has a content of 20 to 50 g/l of chloride ions and 1 to 7 g/l of ammonia with a pH value of 9.5 to 11.5 and a temperature of 45 to 60°C. The molar ratio of chloride ions to ammonia should preferably be from 2 to 10.

Sodium sulfate may additionally be added to the electrolyte in order to dope the product with sulfate.

The electrolysis brine preferably exhibits a pH value of below 11, particularly preferably between 10 and 10.5 (at reaction temperature). The chloride ion concentration is provided by an aqueous solution of alkali metal chlorides. The pH value is established by apportioning an alkali metal hydroxide solution or hydrochloric acid as a function of continuous pH measurement.

According to the invention, a "completely intermixed electrolysis cell" is taken to mean a single electrolysis cell in which the anode and cathode are in contact with substantially the same brine, *i.e.* in which there is no structural separation of the cell volume into an anode and a cathode compartment by diaphragms or membranes. This disregards the membrane function of the deposits of basic nickel salt formed *in situ*. According to the invention, "completely intermixed" furthermore means that, with the exception of boundary layer effects in the vicinity of the anode surfaces, the

brine itself is of a uniform composition, which is ensured by turbulent intermixing. This is achieved by continuously withdrawing brine from the electrolysis cell by means of a piping system comprising a pump and arranged outside the cell and returning the brine to the cell, *i.e.* the brine is recirculated through the electrolysis cell. The brine recirculation rate is preferably at least 100 times the filling volume of the cell, in particular more than 200 times and particularly preferably 400 to 1000 times the filling volume of the electrolysis cell. The elevated recirculation rate in the cell of at least 20 cm/s ensures that the same brine parameters prevail in the electrolysis cell as in the recirculation circuit outside the cell. The elevated recirculation rate in particular ensures that the increase in temperature of the brine is minimal on a single passage. Temperature control is provided by a heat exchanger arranged in the recirculation circuit outside the cell.

Hydrogen deposited at the cathode is produced as the secondary product of the process and is withdrawn from the cell above the brine. The dispersed hydrogen bubbles provide additional turbulent mixing of the brine.

The average residence time of the brine is for example 3 to 5 hours, *i.e.* some $\frac{1}{3}$ to $\frac{1}{5}$ respectively of the filling volume of the cell is discharged from the recirculation circuit each hour, the nickel hydroxide particles are separated from the discharged brine and the brine returned to the recirculation circuit.

The nickel hydroxide particles may be separated by filtration or by using centrifugal forces, for example in a centrifugal decanter. The separated nickel hydroxide is then washed first with completely deionised water, then with dilute, for example 1 molar, sodium hydroxide solution and then again with completely deionised water before subsequently being dried.

Electrolytic dissolution of the nickel is preferably performed at a current density of 500 to 2000 A/m². Depending upon electrode spacing, the requisite voltage is 2.2 to 4 volts. Anodic faradaic current yield of greater than 98% is achieved.

Doped nickel hydroxide is preferably produced for use in rechargeable alkaline storage batteries. Doping elements which may in particular be considered are cobalt, zinc, cadmium, magnesium, aluminium, copper, chromium, iron, scandium, yttrium, lanthanum, lanthanoids, boron, gallium or manganese. The doping elements are continuously introduced, preferably into the recirculation circuit outside the cell, preferably in the form of the aqueous chlorides thereof, in particular in a quantity ratio relative to the electrolytically dissolved nickel corresponding to the subsequent doping rate. It is furthermore necessary simultaneously to introduce an appropriate quantity of ammonia in order to maintain the ammonia/chloride ratio. Sodium hydroxide solution or hydrochloric acid are added appropriately on the basis of pH value control. In the described process for the production of doped nickel hydroxides, neutral salts are accordingly obtained substantially only in stoichiometric quantities corresponding to the quantity of doping. This formation of neutral salts may also be avoided by additional anodes of the doping metals or by pre-alloying the nickel anode with the doping elements.

According to another embodiment of the invention, doped nickel hydroxides are produced by using nickel anodes alloyed with the doping elements.

Nickel hydroxides coated with cobalt hydroxide are produced according to another embodiment of the invention. To this end, the brine containing nickel hydroxide discharged from the recirculation circuit of the electrolysis cell is preferably introduced into another electrolysis cell having anodes consisting of cobalt. This downstream electrolysis cell, in which the nickel hydroxide is coated with cobalt(II) hydroxide, is operated under substantially identical conditions as the upstream electrolysis cell for producing nickel hydroxide. The ratio of the anode areas (at an identical current density) is here selected such that the desired molar ratio of nickel hydroxide core and cobalt hydroxide coating is produced. Once the brine containing nickel hydroxide particles coated with cobalt hydroxide has been separated from the recirculation circuit of the downstream electrolysis cell with a cobalt anode and the

solid particles have been further removed from the brine, the brine is returned to the first recirculation circuit for the production of the nickel hydroxide.

5 According to another preferred embodiment of the invention, the nickel hydroxide is discharged from the recirculation circuit of the first electrolysis cell in concentrated form by means of a centrifuge, wherein the smaller nickel hydroxide crystals remain in the returned brine and are returned to the first electrolysis cell. The concentrated suspension containing nickel hydroxide particles is introduced into the substantially separate recirculation circuit of the downstream electrolysis cell with a cobalt electrode. Particularly uniform nickel hydroxide particles may be produced in this manner.

The invention is illustrated in greater detail below by means of Figures 1 to 4:

- 15 Figure 1 shows a first embodiment of the invention for the production of doped or undoped nickel hydroxide.
- Figure 2 shows an apparatus according to the invention for the production of nickel hydroxide coated with cobalt hydroxide.
- 20 Figure 3 shows an apparatus according to the invention for the production of coated nickel hydroxide having a particularly uniform particle size distribution.
- 25 Figure 4 shows an SEM micrograph of the nickel hydroxide produced according the Example.

Figure 1 shows an electrolysis cell 1, which contains a cathode 2 and an anode 3. The electrolysis brine in the bottom of the cell 1 is recirculated via the pump 4, the heat exchanger 5 and the pH probe 6. As indicated by arrow 7, alkali metal hydroxide or hydrochloric acid is apportioned into the recirculation circuit as a

30

function of the pH measurement 6. Nickel hydroxide suspension is discharged from the recirculation circuit by means of pump 9 and passed to the solids separation apparatus 10. As indicated by arrow 12, the solids are discharged. The brine, from which the solids have been removed, is returned by means of pump 11 into the recirculation circuit via electrolyte reconditioning 16, optionally with addition of water 15. Moreover, as indicated by arrow 8, an inlet is provided by means of which ammonia losses may be made good. Doping salt solutions may furthermore be introduced into the recirculation circuit via the inlet 8a. According to a preferred embodiment, the separation apparatus 10 assumes the form of a screen centrifuge which is operated such that finely divided nickel hydroxide particles are returned to the recirculation circuit with the filtrate via the pump 11. Gaseous hydrogen produced during electrolysis is withdrawn above the filling volume of the cell, as indicated by arrow 13.

Figure 2 shows a first electrolysis cell 1 with a nickel anode 3, wherein the same reference numerals otherwise denote the same elements as in Figure 1. A second electrolysis cell 20 with a cobalt electrode 23 is arranged downstream from electrolysis cell 1. The brine is correspondingly circulated via the pump 24 and heat exchanger 25. The nickel hydroxide suspension discharged via pump 9 from the recirculation circuit of electrolysis cell 1 is introduced into the recirculation circuit. A corresponding quantity of suspension containing nickel hydroxide coated with cobalt hydroxide is discharged via pump 29 and introduced into the evacuating apparatus 30. The filtrate is returned via pump 11 to the recirculation circuit of electrolysis cell 1. The solids separated from the brine are discharged, as indicated by arrow 32, and sent for washing and drying.

Figure 3 shows an embodiment of the invention as in Figure 2, wherein, however, an additional separating centrifuge 42 is provided, by means of which the brine circuits from electrolysis cells 1 and 20 are separated, wherein only the larger nickel hydroxide particles separated with the separating centrifuge 42 are transferred into

the recirculation circuit of electrolysis cell 20 and smaller nickel hydroxide particles are returned to electrolysis cell 1 via the brine of circulating pump 11.

Example

An test setup according to Figure 1 is used. Electrolysis cell 1 has a capacity of 2.3 litres and is equipped with a nickel anode and a nickel cathode, each of an electrode area of 400 cm². The brine circulated in the recirculation circuit contains 44.6 g/l of sodium chloride and 2.6 g/l of ammonia. 48 g of an aqueous doping solution containing 34 g/l of cobalt and 51.5 g/l of zinc in the form of the chlorides thereof are introduced each hour via feed 8a. The pH value is adjusted to 10.3 at a brine temperature of 55°C by introducing 1 molar sodium hydroxide solution via feed 7. A steady-state NH₃ concentration is maintained by introducing approx. 10 ml/h of NH₃ solution (50 g of NH₃/l) via feed 8. The current density in the electrolysis cell is 1000 A/m². 43.8 g of nickel are anodically oxidised each hour. The voltage between the electrodes is approx. 2 volts. The nickel hydroxide discharged at 12 is washed first with completely deionised water, then with 1 molar sodium hydroxide solution and then again with completely deionised water and dried in a circulating air drying cabinet at a temperature of 70°C. The hourly yield is 76 g.

Analysis reveals a product containing 57.5 wt.% of nickel, 1.95 wt.% of cobalt, 2.94 wt.% of zinc, 17 ppm of sodium, 300 ppm of chlorine and having an ammonia content of less than 40 ppm.

The tap density of the product is 2.1 g/cm³, the BET specific surface area 15.6 m²/g and the average particle size 3.1 µm (Mastersizer D50).

Figure 4 shows an SEM micrograph of the spherical nickel hydroxide.

Crystallite size, determined radiographically, is 69 Å, FWHM is 0.92°2θ.

Battery testing to AWTB/3rd discharge cycle reveals a specific capacity of 270 mAh, corresponding to Ni-SES (single-electron-step) utilisation of 103%.

Patent Claims

1. Process for the production of spherical nickel hydroxide by anodic dissolution of a nickel electrode and precipitation of nickel hydroxide in a completely intermixed electrolysis cell, characterised in that an electrolysis brine is used which has a content of 20 to 50 g/l of chloride ions and 1 to 7 g/l of ammonia with a pH value of 9.5 to 11.5 and a temperature of 45 to 60°C.
2. Process according to claim 1, characterised in that, before introduction into the electrolysis cell, the electrolysis brine is adjusted to a pH value of 10 to 10.5 by addition of alkali metal hydroxide or hydrochloric acid.
3. Process according to claim 1 or 2, characterised in that the circulation rate of the brine is at least 20 cm/s.
4. Process according to any one of claims 1 to 3, characterised in that the molar ratio of chloride ions to ammonia is 2 to 10.
5. Process according to any one of claims 1 to 4, characterised in that the average residence time of the electrolysis brine in the cell is 1 to 5 hours.
6. Process according to any one of claims 1 to 5, characterised in that one or more doping metal ions from the group comprising Co, Zn, Mg, Cu, Cr, Fe, Sc, Y, La, lanthanoids, B, Ga, Mn, Cd and Al are continuously introduced into the electrolysis.
7. Process according to any one of claims 1 to 6, characterised in that brine containing dispersed nickel hydroxide powder is discharged from the cell, the nickel hydroxide powder is separated and the brine is returned to the electrolysis cell.

- 5 8. Process according to any one of claims 1 to 7, characterised in that brine containing dispersed nickel hydroxide powder is discharged from the electrolysis cell and introduced into a downstream electrolysis cell, wherein the further electrolysis cell has anodes made of metallic cobalt.
- 10 9. Process according to claim 8, characterised in that brine containing nickel hydroxide powder coated with cobalt hydroxide is discharged from the electrolysis cell containing metallic cobalt, the nickel hydroxide powder is separated and the brine is returned to the electrolysis cell with nickel electrodes.
- 15 10. Process according to claim 6, characterised in that the doping element ions are produced by anodic oxidation of the corresponding metals.
11. Use of the nickel hydroxide powder produced according to any one of claims 1 to 10 as an electrode material in secondary storage batteries.
- 20 12. Use of the nickel hydroxide powder produced according to any one of claims 1 to 10 as a precursor material for the production of ultrafine powdered metallic nickel.

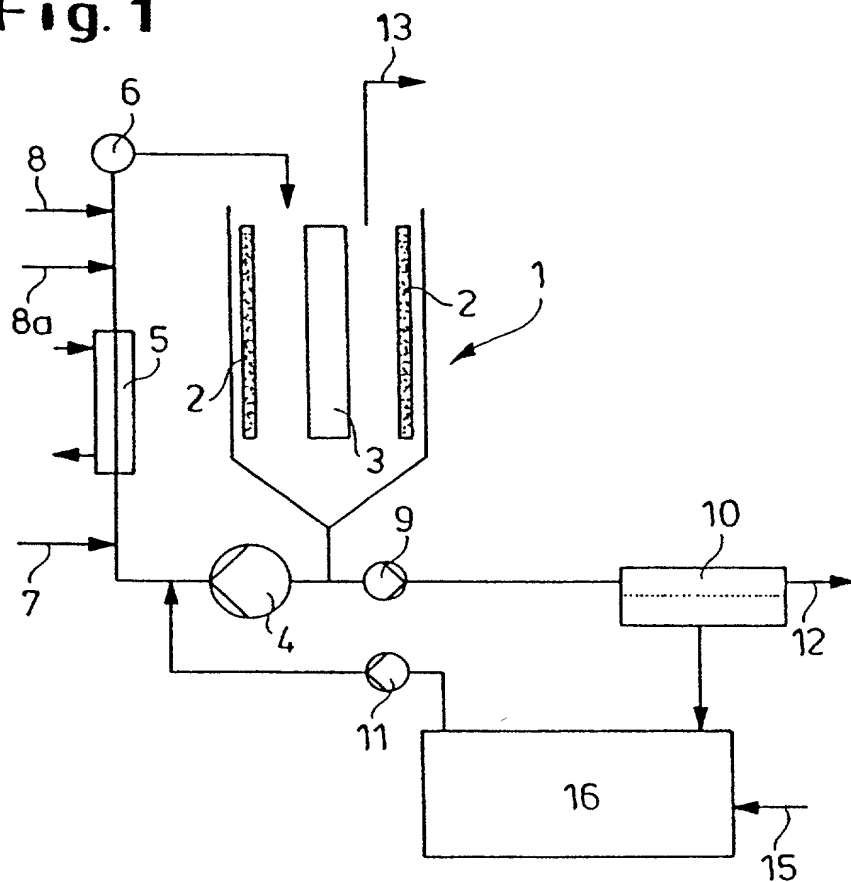
Fig. 1

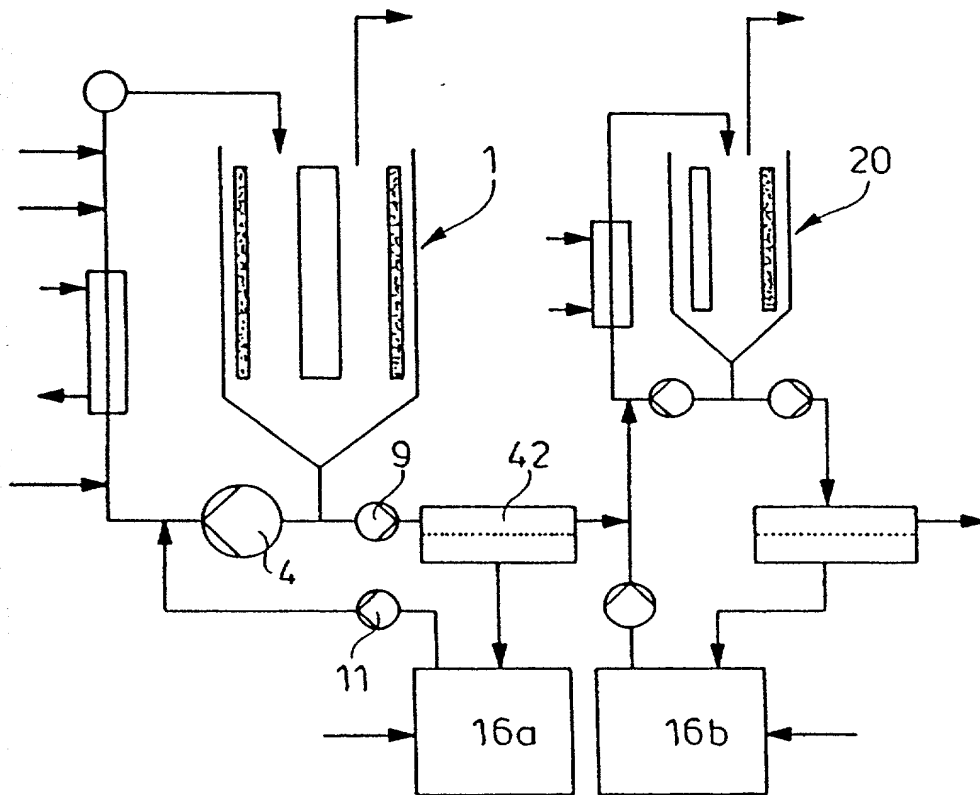
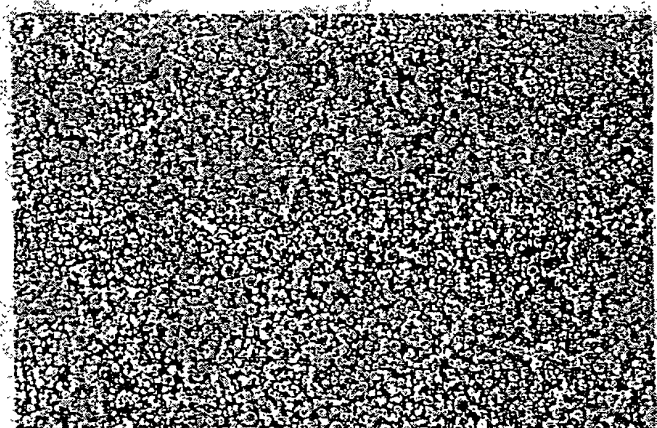
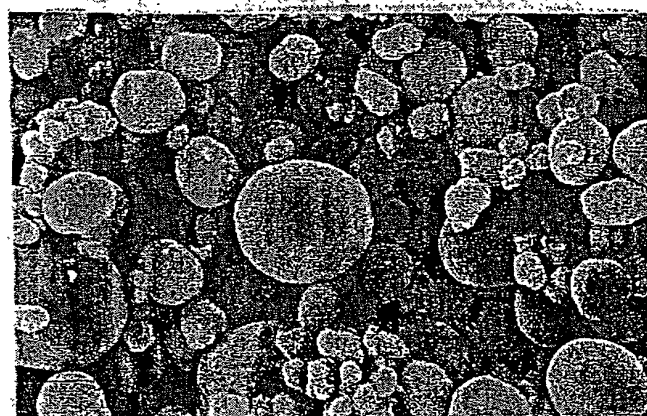
Fig. 3

Fig 4

00001240

30 μm

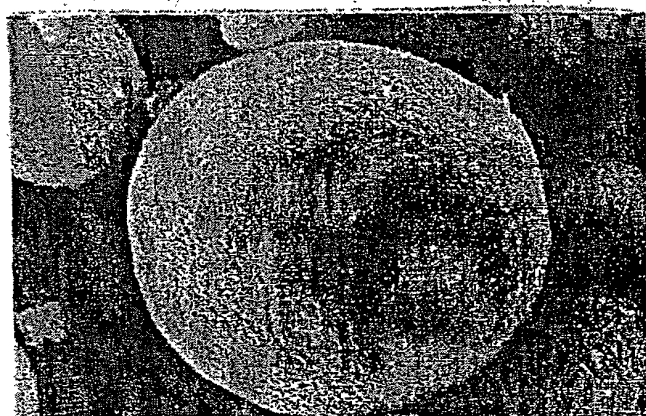
HCST



00001241

3 μm

HCST



00001242

1 μm

HCST

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR PRODUCING NICKEL HYDROXIDES

the specification of which is attached hereto,

or was filed on **April 25, 2000**

as a PCT Application Serial No. **PCT/EP00/03684**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 21 313.5	Germany	May 7, 1999
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

STA 144-US

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,
Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619
GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office
Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138
DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office
Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: Direct Telephone Calls To:

Patent Department

Bayer Corporation (412) 777-2349

100 Bayer Road

Pittsburgh, Pennsylvania 15205-9741

FULL NAME OF SOLE OR FIRST INVENTOR Armin Olbrich		INVENTOR'S SIGNATURE <i>Armin Olbrich</i>	DATE 12.9.2001
RESIDENCE D 38723 Seesen, Germany <i>DEX</i>		CITIZENSHIP German	
POST OFFICE ADDRESS Alte Dorfstr. 20, D 38723 Seesen, Germany			
FULL NAME OF SECOND INVENTOR Viktor Stoller		INVENTOR'S SIGNATURE <i>Viktor Stoller</i>	DATE 12.9.2001
RESIDENCE D 38667 Bad Harzburg, Germany <i>DEX</i>		CITIZENSHIP German	
POST OFFICE ADDRESS Am Wildpark 17, D 38667 Bad Harzburg, Germany			
FULL NAME OF THIRD INVENTOR Juliane Meese-Marktscheffel		INVENTOR'S SIGNATURE <i>Juliane Meese-Marktscheffel</i>	DATE 12.9.2001
RESIDENCE D 38640 Goslar, Germany <i>DEX</i>		CITIZENSHIP German	
POST OFFICE ADDRESS Nußanger 8, D 38640 Goslar, Germany			
FULL NAME OF FOURTH INVENTOR Frank Schruppf		INVENTOR'S SIGNATURE <i>Frank Schruppf</i>	DATE 21.09.2001
RESIDENCE D 38642 Goslar, Germany <i>DEX</i>		CITIZENSHIP German	
POST OFFICE ADDRESS Lorenz-Biggen-Weg 5, D 38642 Goslar, Germany			
FULL NAME OF FIFTH INVENTOR Josef Schmoll		INVENTOR'S SIGNATURE <i>Josef Schmoll</i>	DATE 24.09.01
RESIDENCE D 38642 Goslar, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Rudolf-Nickel-Weg 3, D 38642 Goslar, Germany <i>DEX</i>			
FULL NAME OF SIXTH INVENTOR Gerhard Gille		INVENTOR'S SIGNATURE <i>Gerhard Gille</i>	DATE 11.09.01
RESIDENCE D 38640 Goslar, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Spitalstr. 8, D 38640 Goslar, Germany <i>DEX</i>			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			